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(21) International Application Number: PCT/US96/20537 (22) International Filing Date: 17 December 1996 (17.12.96) (30) Priority Data: 08/579,042 21 December 1995 (21.12.95) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: RAIFORD, Kimberly, Gheysen; 571 Mildred Road, Fayetteville, NC 28314-2529 (US). LISS, Theodor, Arthur; 105 Rockingham Drive, Wilmington, DE 19803-2615 (US). GREENWOOD, Edward, James; 23 Raphael Road, Hockessin, DE 19707-2209 (US). (74) Agent: MAYER, Nancy, S.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).	(81) Designated States: AU, CA, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: FLUORINATED ESTER MELT ADDITIVES FOR THERMOPLASTIC FIBERS (57) Abstract A composition having repellency to low surface tension fluids comprising a material prepared by forming a mixture of a polymer selected from the group consisting of polyolefin, polyamide, polyester, polyacrylate, and blends and copolymers thereof, and a fluorochemical compound comprising a fluorocarbon/hydrocarbon ester of the formulae: $R_f-O-C(O)-R_1$ or $R_f-C(O)-O-R_1$ wherein R_f is selected from the group consisting of: 1) $F(CF_2)_x-(CH_2)_m$ wherein x is from about 4 to about 20 and m is from about 0 to about 6; and 2) $F(CF_2)_x-SO_2N(R_2)-R_3$ where x is a positive integer from about 4 to about 20, R_2 is an alkyl radical of from about 1 to about 4 carbon atoms, R_3 is an alkylene radical of from about 1 to about 12 carbon atoms; and R_1 is an aliphatic hydrocarbon having from about 12 to about 76 carbon atoms; and provided that said fluorochemical compound is other than perfluoroalkylethyl stearate; and melt extruding the mixture.		

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TITLE

FLUORINATED ESTER MELT ADDITIVES FOR THERMOPLASTIC FIBERS

FIELD OF THE INVENTION

5 This invention relates to a process for imparting superior repellency of low surface tension fluids to thermoplastic polymers, in particular fibers, fabrics, nonwovens, films and molded articles by the addition of certain fluorinated esters to the polymer melt.

BACKGROUND OF THE INVENTION

10 Thermoplastic polymer fibers are frequently treated with fluorochemical compounds in order to affect the surface characteristics of the fiber, for example to improve water repellency or to impart stain or dry soil resistance. Most
15 frequently, fluorochemical dispersions are applied topically to the fabrics made from these fibers by spraying, padding or foaming, followed by a drying step to remove water.

 For example, a method is known for obtaining dry soil resistance and nonflame propagating characteristics in a
20 textile fiber by applying topically aqueous dispersions of a variety of fluorinated esters derived from perfluoroalkyl aliphatic alcohols of the formula $C_nF_{2n+1}(CH_2)_mOH$ where n is from about 3 to 14 and m is 1 to 3, together with mono- or polycarboxylic acids which contain from 3 to 30 carbons and
25 can contain other substituents. The fluorinated esters include, among others, a perfluoroalkylethyl stearate corresponding to "ZONYL" FTS, as well as perfluoroalkylethyl diesters made from dodecanedioic acid or tridecanedioic acid.

 It is well recognized that the process of
30 manufacturing thermoplastic polymeric fibers and fabrics could be simplified and significant capital investment could be eliminated if the topical application were replaced by incorporating a fluorochemical additive into the polymer melt prior to the extrusion of the fiber. The difficulty has been
35 in finding suitably effective fluorochemical additives.

 Thermoplastic polymers include, among others, polyolefins, polyesters, polyamides and polyacrylates. Polyolefins, and in particular polypropylene, are frequently

used for disposable nonwoven protective garments, particularly in the medical/surgical field, in part because of a polyolefin's inherent water-repellency. However, polyolefins are not inherently good repellents for other lower surface tension fluids frequently encountered in the medical field such as blood and isopropyl alcohol. To get around this deficiency, fluorochemical dispersions are applied topically to these fabrics.

The requirements of an additive suitable for incorporating into a polyolefin melt include, besides the ability to repel low surface tension fluids at a low concentration of the additive, a satisfactory thermal stability and low volatility to withstand processing conditions. Preferably the compound will migrate to the surface of the fiber so as to minimize the amount of additive needed for adequate repellency. While this migration can often be enhanced by post-extrusion heating of the fiber, it is more preferable for the migration to occur without the need for this heating step. This requirement for mobility in the polymeric fiber in turn tends to limit the size of the fluorochemical molecule, and effectively eliminates from consideration high molecular weight polymeric fluorochemical additives.

The general concept of incorporating fluorochemical additives into a polyolefin fiber melt is known, but the difficulty in finding suitable effective additives has limited the application of this concept. Many of the past efforts to evaluate such fluorochemical additives have been aimed at improving other properties of the polyolefin, and do not teach methods of its improving repellency to low surface tension fluids.

Nonwoven composite structures are known consisting in part of two or more melt-extruded nonwoven layers, at least one of which includes an additive which imparts to the surface at least one characteristic different than the surface characteristics of the polymer alone as a result of preferential migration of the additive to the surface without the need for post-formation treatment of any kind. Examples

of the additive-including layer include polypropylene modified by commercially available fluorochemical additives, including "ZONYL" FTS defined above.

U.S. Patent 5,178,931 and U.S. Patent 5,178,932
5 disclose specific nonwoven laminiferous and composite structures respectively, consisting in part of three melt-extruded nonwoven layers, the second of which includes an additive which imparts alcohol repellency as a result of preferential migration of the additive to the surface without
10 the need for post-formation treatment of any kind, and where at least one of the first and third layers has been treated by topical application of an agent to change its characteristics in some way. Examples of the additive-including second layer include commercially available fluorochemicals, including
15 "ZONYL" FTS.

Soil resistant polymeric compositions are known which are prepared by melt extrusion with a nonpolymeric fluorochemical dispersed throughout the polymer. The polymers used include polypropylene, polyethylene, polyamide and
20 polyester, and the fluorochemical used is a perfluoroalkylstearate, in particular "ZONYL" FTS.

In addition, a polymeric composition is known comprising a mixture of a polymer selected from the group of polypropylene, polyethylene, polyamide and polyester with a
25 fluorochemical comprising a fluorinated oleophobic, hydrophobic alkyl group attached to a nonfluorinated oleophilic alkyl, aryl, aralkyl or alkaryl moiety optionally through a linking moiety, which can be melt extruded as a mixture. A more specific description of the above
30 fluorochemical is not disclosed, but among the many compounds which are applicable are esters where the oleophilic organic group contains from 2 to 35 carbon atoms. Examples of such are "ZONYL" FTS or a product made by transesterifying "ZONYL" BA with methyl stearate and methyl palmitate.

35 An automotive coating film is known containing an organic solvent-soluble waxy hydrocarbon which possesses a fluorine-containing organic group. This component is a product obtained by esterifying and coupling a high molecular weight

alcohol with a carboxylic acid which possesses a fluorine-containing group or a product obtained by esterifying and coupling a high molecular weight fatty acid and an alcohol which possesses a fluorine-containing group. As examples of high molecular weight alcohols included are those with average carbon chain lengths with up to 50 carbons. As examples of high molecular weight fatty acids included are those with carbon chain lengths of up to 31 carbons (mellitic acid). The products were tested only as a waxing agent for automobiles.

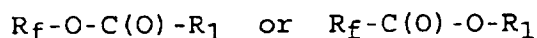
Japanese Patent Application 3-41160 to Kao Corp. teaches a thermoplastic resin composition containing a perfluoroalkyl group-containing long chain fatty ester of the formula $R_f-R_1-OCO-R_2$ where R_f is a perfluoroalkyl group with 5 to 16 carbons, R_1 is an alkylene group with 1 to 4 carbons, and R_2 is an unsaturated alkyl group or a saturated alkyl group with 21 to 50 carbons. One example reacts $C_8F_{17}C_2H_4OH$ with $C_{27}H_{55}COOH$ to produce the ester. The resins included polyethylene and polypropylene. Benefits of the additive were shown by the contact angle of water with molded articles of the resin. No tests are reported on the repellency to low surface tension fluids of the resulting polymers.

In summary, while the prior art discloses numerous examples of polyolefin fibers containing a fluorochemical additive incorporated at the melt stage to alter the surface characteristics of the extruded fiber, much of this was aimed at soiling and staining resistance, water repellency or other purposes. Those references which were aimed at imparting alcohol repellency to polyolefin fabrics employ "ZONYL" FTS. A need exists to achieve superior repellency to low surface tension fluids and superior product efficiency. The fluorinated compounds of the present invention meet this need.

SUMMARY OF THE INVENTION

The present invention comprises a composition and a process for imparting repellency of low surface tension fluids to thermoplastic polymer articles. The composition having
5 repellency to low surface tension fluids of the present invention comprises a material prepared by:

forming a mixture of a polymer selected from the group consisting of polyolefin, polyamide, polyester, polyacrylate, and blends and copolymers thereof, and a
10 fluorochemical compound comprising a fluorocarbon/hydrocarbon ester of the formulae:



wherein R_f is selected from the group consisting of 1) $F(CF_2)_x-(CH_2)_m$ wherein x is from about 4 to about 20 and m is
15 from about 0 to about 6, and 2) $F(CF_2)_x-SO_2N(R_2)-R_3$ wherein x is a positive integer from about 4 to about 20, R_2 is an alkyl radical of from 1 to about 4 carbon atoms, and R_3 is an alkylene radical of from 1 to about 12 carbon atoms and R_1 is an aliphatic hydrocarbon of from about 12 to about 76 carbon
20 atoms; provided that said fluorochemical compound is other than perfluoroalkylethyl stearate; and melt extruding the mixture.

The present invention further comprises the above composition in the form of a filament, fiber, nonwoven fabric
25 or web, film or molded article.

The present invention further comprises a process for imparting repellency of low surface tension fluids to a thermoplastic polymer article comprising forming a mixture prior to article formation of a polymer and an effective
30 amount of a fluorochemical compound comprising a fluorocarbon/hydrocarbon ester as defined above and melt extruding the mixture. Such articles include filaments, fibers, nonwoven webs or fabrics, films or molded articles.

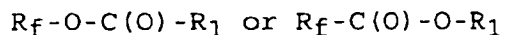
DETAILED DESCRIPTION OF THE INVENTION

35 Superior repellency to low surface tension fluids is imparted to thermoplastic polymer articles, in particular fibers, fabrics, filaments, nonwovens, films, and molded articles, by the addition of certain monomeric fluorinated

ester compounds to a polymer prior to article formation and melt extruding the resulting mixture. This process is used either with or without post-extrusion heating of the article to promote movement of the additive to the article surface, since the ester compounds of this invention tend by their nature to concentrate on the surface.

The term "low surface tension fluids" is used herein to mean fluids having a surface tension of less than 50 dynes/cm (50×10^{-7} newton metre). Examples of such fluids include alcohols, blood, and certain body fluids.

The composition of the present invention comprises a material prepared by melt extruding a mixture of a polymer selected from the group consisting of polyolefin, polyamide, polyester, polyacrylate, and blends and copolymers thereof, and a fluorochemical compound, other than perfluoroalkylethyl stearate, comprising a fluorocarbon/hydrocarbon ester of the formulae:



wherein R_f in the above formulas is $F(CF_2)_x-(CH_2)_m$ wherein x has a preferred average value of about 7 to 10 and a range of about 4 to about 20 and m has a value of 0 to 6.

Especially preferred for R_f is a composition wherein the chain length distribution is as follows:

$x=6$ or less	0-10% by weight
$x=8$	45-75% by weight
$x=10$	20-40% by weight
$x=12$	1-20% by weight
$x=14$ or greater	0-5% by weight.

This composition range, when $m=2$, and x has an average value of about 9, is hereinafter referred to as Telomer BN. This definition of R_f in the formula R_f-OH is referred to as Telomer BN alcohol.

Alternatively R_f is a fluorinated sulfonamide of the structure $F(CF_2)_x-SO_2N(R_2)-R_3$ wherein x is a positive integer from about 4 to about 20, preferably 4 to 10 inclusive, R_2 is an alkyl radical having from 1 to 4 carbon atoms, and R_3 is an alkylene radical having from 1 to 12 carbon atoms. Preferably R_2 is CH_3 and R_3 is $-CH_2CH_2-$, $-(CH_2)_3-$, or $-(CH_2)_4-$.

The fluoroalkyl portion of the alternative R_f structure is a fluorinated, preferably saturated, monovalent, non-aromatic, aliphatic radical of at least three fully fluorinated connected carbon atoms in a chain. The chain in
5 the radical is straight, branched, or, if sufficiently large, cyclic and is optionally interrupted by divalent oxygen atoms, hexavalent sulfur atoms, or trivalent nitrogen atoms bonded only to carbon atoms. A fully fluorinated aliphatic radical is preferred, but hydrogen or chlorine atoms are optionally
10 present as substituents in the radical provided that not more than one atom of either is present in the radical for every two carbon atoms.

R_1 is an aliphatic hydrocarbon with a carbon chain length of about 12 to about 76 carbons, preferably from about
15 24 to about 50 carbons. Alcohols corresponding to R_1 -OH are commercially available from Petrolite Corporation, Polymer Division Headquarters, 6910 E. 14th Street, Tulsa, Oklahoma, USA 74112, under the trademark "UNILIN". "UNILIN" alcohols are fully saturated long chain linear alcohols. The
20 approximate R_1 ranges of "UNILIN" 350, 425, 550 and 700 are 12 to 50, 14 to 58, 16 to 56 and 14 to 66, respectively. The average chain lengths for "UNILIN" 350, 425, 550 and 700 are about 24, 32, 40 and 48, respectively. These are preferred for use in the present invention. Acids corresponding to R_1 -
25 COOH are commercially available from Petrolite Corporation, Polymers Division Headquarters, 6910 E. 14th Street, Tulsa, Oklahoma, 74112, under the trademark "UNICID". The range of average chain lengths for "UNICID" 350, 425, 550 and 700 are 24-29, 29-37, 37-45 and 40-48, respectively. These are
30 preferred for use in the present invention. More particularly the "UNILIN" and "UNICID" carbon chain lengths are as noted in Table A.

TABLE AGC DATA**

	<u>UNILIN</u>	<u>Lit. Avg.*</u>	<u>% Alcohol</u>	<u>Range</u>	<u>Average</u>
	350	C24-26		C12-46	C24-26
5	425	C30-32	85.0	C14-58	C30-32
	550	C40-42	79.5	C16-56	C38
	700	C48-50	83.6	C14-66	C50

GC DATA**

	<u>UNICID</u>	<u>Lit. Avg.*</u>	<u>% Acid</u>	<u>Range</u>	<u>Average</u>
10	350	C24-29	79.0	C12-50	C28-30
	425	C29-37			
	550	C37-45	80.0	C16-62	C42-44
	700	C40-48		C16-76	

* Literature average

15 **Gas chromatography data

There are various methods by which the above compounds can be prepared, and the inventive process is not limited to a particular method of preparation. For example, the above compounds are conveniently made by reacting an appropriate fatty alcohol with the appropriate fluorocarbon acid to form an acid ester, or by reacting an appropriate fatty acid with the appropriate fluorocarbon alcohol. Other compounds in these groups are readily made by those skilled in the art by following similar processes.

25 The esters useful in this invention are mixed with thermoplastic polymers by adding them to pelletized, granular, powdered or other appropriate forms of the polymers and rolling, agitating or compounding the mixture to achieve a uniform mixture which is then melt extruded. Alternatively

30 the esters are added to a polymer melt to form a mixture which is then melt extruded. The thermoplastic polymer is a polyolefin, polyester, polyamide, or polyacrylate. The thermoplastic polymer preferably is a polyolefin, mixture or blend of one or more polyolefins, a polyolefin copolymer,

35 mixture of polyolefin copolymers, or a mixture of at least one polyolefin and at least one polyolefin copolymer. The thermoplastic polymer is more preferably a polyolefin polymer or copolymer wherein the polymer unit or copolymer unit is ethylene, propylene or butylene or mixtures thereof. Thus the

polyolefin is preferably polypropylene, polyethylene, polybutylene or a blend or copolymer thereof.

The amount of the fluorinated compound to be added to the thermoplastic polymer is preferably between 0.1 and about 5% by weight of the polymer. Amounts above this range can be used but are unnecessarily expensive in relation to the benefit received. The blend is then melted and extruded into fibers, filaments, nonwoven webs or fabrics, films, or molded articles using known methods. The fluorine content of the fiber, filament, nonwoven fabric or web prepared therefrom, film or molded article is from about 200 ug/g to about 25,000 ug/g.

Extrusion is used to form various types of nonwovens. In particular, extrusion is used to form a melt blown nonwoven web of continuous and randomly deposited microfibers having an average diameter of approximately 0.1 to 10 microns, preferably in the range of about 3 to 5 microns. The melt extrusion is carried out through a die at a resin flow rate of at least 0.1 to 5 grams per minute per hole, with the microfibers being randomly deposited on a moving support to form the web.

In the above melt blowing process, polymer and a compound of the present invention are fed into an extruder where it is melted and passed through a die containing a row of tiny orifices. As the polymer emerges from the die, it is contacted by two converging, high-velocity hot air streams, which attenuate the polymer into a blast of fine, discontinuous fibers of 0.1 to 10 microns in diameter. The useful polymer throughputs or flow rates range from 0.1 to 5 grams per minute per hole. Typical gas flow rates range from 2.5 to 100 pounds per square inch (1.72×10^5 to 6.89×10^5 Pa) per minute of gas outlet area. The air temperature ranges from about 400°F (204°C) to 750°F (399°C). Cooling air then quenches the fibers, and they are deposited as a random, entangled web on a moving screen which is placed 6 to 12 inches (15.2 to 30.5 cm) in front of the blast of fibers.

Melt blowing processes are described in further detail in articles by V. A. Wentz, "Superfine Thermoplastic

Fibers", Industrial and Engineering Chemistry, Vol. 48(8), pp 1342-1346 (1956); and by R. R. Buntin and D. T. Lohkamp, "Melt Blowing - A One-step Web Process for New Nonwoven Products", Journal of the Technical Association of the Pulp and Paper Industry, Vol. 56(4), pp 74-77 (1973); as well as in U.S. Patent 3,972,759 to R. R. Buntin. The disclosures of these documents are hereby incorporated by reference.

The unique properties of a melt blown nonwoven web comprised of a random array of fine, entangled fibers include very large surface areas, very small pore sizes, moderate strength and light weight fabric structure. These properties make the nonwoven webs particularly suitable for such applications as medical fabrics where barrier properties as well as breathability and drape are important.

Extrusion is also used to form polymeric films. In film applications, a film forming polymer is simultaneously melted and mixed as it is conveyed through the extruder by a rotating screw or screws and then is forced out through a slot or flat die, for example, where the film is quenched by a variety of techniques known to those skilled in the art. The films optionally are oriented prior to quenching by drawing or stretching the film at elevated temperatures.

Molded articles are produced by pressing or by injecting molten polymer from a melt extruder as described above into a mold where the polymer solidifies. Typical melt forming techniques include injection molding, blow molding, compression molding and extrusion, and are well known to those skilled in the art. The molded article is then ejected from the mold and optionally heat-treated to effect migration of the polymer additives to the surface of the article.

An optional heating or annealing step can be conducted but is not required. The polymer melt or extruded fiber, filament, nonwoven web or fabric, film, or molded article is heated to a temperature of from about 25°C to about 150°C. The heating in some cases may improve the effectiveness of the fluorochemical additive in imparting alcohol repellency.

The compositions of the present invention are useful in various fibers, filaments, nonwoven webs or fabrics, films and molded articles. Examples include fibers for use in fabrics and carpets, nonwoven fabrics used in protective garments used in the medical/surgical field, and molded plastic articles of many types. The process of the present invention is useful for imparting repellency of low surface tension fluids to various thermoplastic polymer articles such as filaments, fibers, nonwoven webs or fabrics, films and molded articles.

Example 1

Synthesis of $R_f-O-C(O)-R_1$, wherein R_f is an aliphatic fluorocarbon radical of formula $F(CF_2)_x(CH_2)_m$ where the average value of x is 9, $m=2$, and wherein R_1 has an average value of 32 carbon atoms.

A 250-mL flask was fitted with a mechanical stirrer, temperature control device, Dean-Stark trap, water condenser, nitrogen gas inlet tube and heating mantle. Into the flask were charged 79.1g (0.15 mole) $F(CF_2)_nCH_2CH_2OH$ where $n=6-18$, avg. $n=9$ and 89.4g (0.15 mole) "UNICID" 425 Acid ($C_{29}-C_{37}$ aliphatic acid from Petrolite Corporation, 6910 E. 14th Street, Tulsa, Oklahoma, USA, 74112, acid no. = 94 mgKOH/g). The mixture was heated and held at 120°C. When the mixture was homogeneous, 0.3g phosphorous acid and 0.12g boric acid were added. The temperature was raised to 140-145°C and held for approximately 87 hours with continuous removal of water. When a gas chromatographic analysis of the reaction mixture indicated that all telomer BN alcohol had reacted, the mixture was cooled slightly and discharged yielding 44.65g (87%) of product. Infrared analysis confirmed the above structure. The product was a tan solid and melted at 66.65°C by Differential Scanning Calorimetry (DSC). The percent fluorine found by analysis was 32.4 % compared to a theoretical analysis of 33.4%.

Examples 2-15

These examples were prepared using the procedure of Example 1. Table 2 lists the acid from which the fluoroester was prepared and the fluorocarbon distribution of the alcohol. All examples were used to prepare melt blown nonwoven webs and tested for alcohol repellency as described in Example 16:

Example 16

Step 1: Preparation of the polymer blend

Uniform mixtures of the fluorochemical additives produced in Examples 1-16 together with a polyolefin were prepared by combining them and rolling the mixture for about 24 hours. Comparative examples A-D used the monoester "ZONYL" FTS and were prepared in a similar manner. In particular, for the compound of Example 4, a uniform mixture of 16.1g (1.2 weight %) of finely ground compound of Example 4, and 1,349g Escorene PD3746G (Exxon Chemical Americas, P.O. Box 3273, Houston, Texas 77001) polypropylene resin having a melt flow rate of approximately 1000 was prepared by rolling the mixture for 24 hours. The fluorine concentration in the mixture was calculated to be 3300 μ g/g fluorine. Actual fluorine concentration in the nonwoven web was 2930 μ g/g fluorine. Comparative examples, designated A-D were prepared in the same manner.

Step 2: Melt blown web formation

Melt blown nonwoven webs were prepared from the above mixtures using a 6-inch (15 cm) melt blowing pilot unit at a polymer feed rate of about 0.4 gram/minute/hole. The polymer blends were fed into the extruder having three barrel zones at temperatures ranging from 175°C to 250°C. The temperature at the die was from 200°C to 260°C and the air temperature at the die varied from 200°C to 270°C. The die tip gap was 0.060 inches (0.15 cm) and the primary air pressure was 2.6 psi (17.9 x 10³ Pa). The webs were formed on a drum coated with

"TEFLON" at an output of 0.4gram/hole/minute and collected on a take-up roll operating at 30 feet/minute(914 cm/minute) which resulted in the fabrics having a basis weight of 1.0 oz./square yard (34 gm/square meter).

5 Step 3. Repellency testing

The water repellent properties of the melt blown webs were measured using an isopropyl alcohol/water test and are expressed in terms of percent isopropyl alcohol rating. Webs that resisted penetration of a 100% isopropyl alcohol/0%
10 water solution (lowest surface tension fluid) after 1-2 minutes were given the highest rating of 100. Webs that are only resistant to a 100% water/0% isopropyl alcohol solution after 1-2 minutes are given the lowest rating of 0. Table 1 lists ratings that correspond to other isopropyl alcohol/water
15 mixtures used in this test. The rating for a given fabric corresponds to the lowest surface tension fluid (greatest % isopropyl alcohol/water solution) that does not wet the fabric after 1-2 minutes.

Table 1
20 Percent Isopropyl Alcohol Ratings

	Rating	%Isopropyl alcohol/%water (vol/vol)
	100	100/0
	90	90/10
	80	80/20
25	70	70/30
	60	60/40
	50	50/50
	40	40/60
	30	30/70
30	20	20/80

To evaluate in-process repellency, the webs were rated immediately after exiting the melt blown line and then after two days and after about one week. Table 2 summarizes the percent isopropyl alcohol data for the polypropylene melt
35 blown webs containing the esters of Examples 1-15 and the

comparison examples A-D containing "ZONYL" FTS available from E. I. du Pont de Nemours and Company, Wilmington, Delaware, at different fluorine concentration levels. Also included in the table is a polypropylene control sample (PP Control).

5 The results in Table 2 showed the clear advantage of the inventive composition over the comparative and control samples, the advantages showing up immediately and over time. A related advantage for the inventive composition is better performance at lower levels of fluorochemical additive.

Table 2
Isopropyl Alcohol Repellency of Polypropylene Melt Blown Webs

Example	Dist ¹	Acid	µg/g Fluorine Target/Actual	As made	Isopropyl alcohol repellency 2 days	1 week	Heated ²
1	BN	"UNICID"	350	1500/1480	40	--	90-100
2	BL	"UNICID"	350	1700/1480	40	--	80
3	BN	"UNICID"	425	3300/2930	90	90-100	90-100
4	BN	"UNICID"	425	3300/3120	40	80	90
5	BN	"UNICID"	550	3300/2720	100	100	100b
6	BN	"UNICID"	550	3300/2790	40	60	90b
7	BN	"UNICID"	550	1980/1910	70-80		100a
8	BL	"UNICID"	550	1980/1570	60	--	92a
9	BN	"UNICID"	700	3300/3210	100	100	100c
10	BN	"UNICID"	700	4500/2760	40	40	100b
11	BN	"UNICID"	700	1980/1780	50-60	80	90
12	BN	Stearic	3300/2940	70	80-90	90-100	80b
13	BN	Stearic	3300/3510	30	60	80	70b
14	M	"UNICID"	550	1980/1550	40	50	50a
15	M	Stearic	1980/1610	30	40	80	30a
A	B	Stearic	3300/3050	70	80-90	90	80b
B	B	Stearic	3300/3010	30	60	80	60-70b
C	B	Stearic	2875/2426	40	80	80	80b
D	B	Stearic	2423/1910	30	70	70-80	80-90b
Control				20	20	20	

1 Fluorocarbon atom distribution: BL=C₄F₉-C₈F₁₇; B=C₄F₉-C₁₈F₃₇; BN= C₈F₁₇-C₁₂F₂₅;
M=C₈F₁₇SO₂N(CH₂H₅) - (CH₂)₂-OH

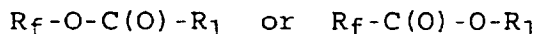
2 Annealing process:

- Web was annealed at 176F (80°C) for 15 seconds shortly after processing
- Web was annealed at 140F (60°C) for 25 hours about one week after processing
- Web was annealed at 180F (82.20°C) for 1 minute shortly after processing

What is claimed is:

1. A composition having repellency to low surface
5 tension fluids comprising a material prepared by:

forming a mixture of a polymer selected from the
group consisting of polyolefin, polyamide, polyester,
polyacrylate, and blends and copolymers thereof, and a
10 fluorochemical compound comprising a fluorocarbon/hydrocarbon
ester of the formulae:



wherein

R_f is selected from the group consisting of:

1) $F(CF_2)_x-(CH_2)_m$ wherein x is from about 4 to about 20 and
15 m is from about 0 to about 6; and

2) $F(CF_2)_x-SO_2N(R_2)-R_3$ wherein x is a positive integer from
about 4 to about 20, R_2 is an alkyl radical of from 1 to about
4 carbon atoms, and R_3 is an alkylene radical of from 1 to
about 12 carbon atoms; and

20 R_1 is an aliphatic hydrocarbon having from about 12 to
about 76 carbon atoms;

provided that said fluorochemical compound is other than
perfluoroalkylethyl stearate;

and melt extruding the mixture.

25

2. The composition of Claim 1 wherein the polymer
is selected from the group consisting of polyolefin, mixture
of polyolefins, polyolefin copolymer, mixture of polyolefin
copolymers, and mixture of at least one polyolefin and at
30 least one polyolefin copolymer.

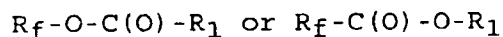
3. The composition of Claim 1 wherein R_f is
 $F(CF_2)_x(CH_2)_m$ wherein x is from about 8 to about 12 and is an
average of about 9, and m is 2.

4. The composition of Claim 1 wherein the
35 fluorochemical is present in an amount of from about 0.1% to
about 5% by weight of the polymer.

5. The composition of Claim 1 having a fluorine content of from about 200 ug/g to about 25,000 ug/g.

6. The composition of Claim 1 in a form selected from the group consisting of an extruded filament, fiber, nonwoven web, nonwoven fabric, film and molded article.

7. A process for imparting repellency of low surface tension fluids to a thermoplastic polymer article comprising forming a mixture prior to article formation of a polymer and an effective amount of a fluorochemical compound comprising a fluorocarbon/hydrocarbon ester of the formulae:



wherein

R_f is selected from the group consisting of:

- 1) $F(CF_2)_x-(CH_2)_m$ wherein x is from about 4 to about 20 and m is from about 0 to about 6; and
- 2) $F(CF_2)_x-SO_2N(R_2)-R_3$ wherein x is a positive integer from about 4 to about 20, R_2 is an alkyl radical of from about 1 to about 4 carbon atoms, and R_3 is an alkylene radical of from about 1 to about 12 carbon atoms; and

R_1 is an aliphatic hydrocarbon having from about 12 to about 76 carbon atoms;

provided that said fluorochemical compound is other than perfluoroalkylethyl stearate;

and melt extruding the mixture.

25

8. The process of Claim 7 further comprising heating the formed article to a temperature of from about 25°C to about 150°C.

30

9. The process of Claim 7 wherein the amount of the fluorochemical compound is from about 0.1% to about 5% by weight of the polymer.

35

10. The process of Claim 7 wherein the article after formation has a fluorine content of from about 200 ug/g to about 25,000 ug/g.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.
PCT/US 96/20537

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/101 D01F1/10 D04H1/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K D01F D04H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 177 (C-0829), 7 May 1991 & JP 03 041160 A (KAO CORP), 21 February 1991, cited in the application see abstract	1-10
X	--- WO 95 01396 A (PEACH STATE LABS INC) 12 January 1995 see page 1, paragraph 1 see page 12, line 31 - page 14, line 27 see page 17, line 25 - line 29; claims -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/20537

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9501396 A	12-01-95	US 5459188 A	17-10-95
		AU 7178394 A	24-01-95
		EP 0708799 A	01-05-96
		US 5560992 A	01-10-96
